

# Lithogeochemical study of some Mendip country rocks with particular reference to boron

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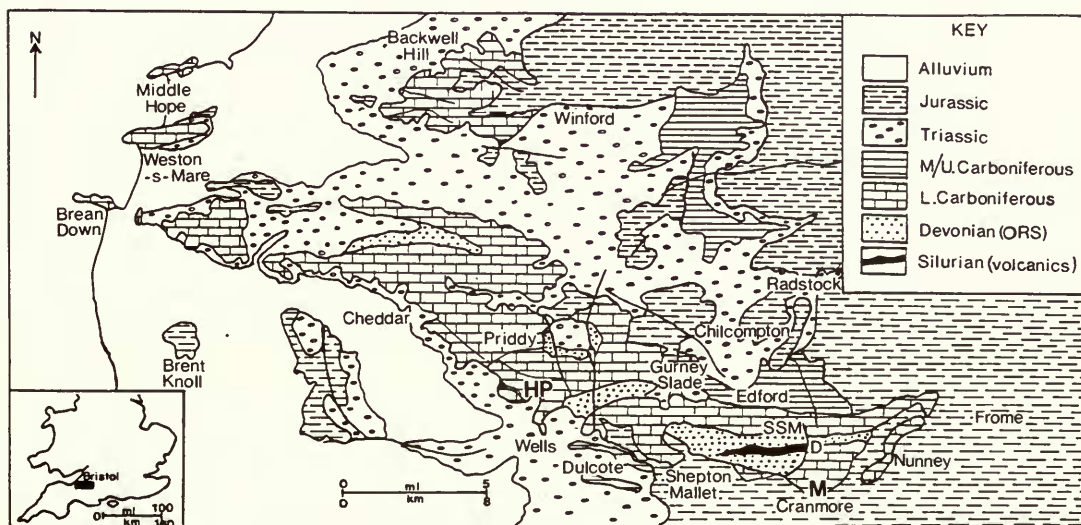
## Synopsis

This report presents quantitative data for 20 elements in 37 samples from the Mendip Hills, Somerset, England. The data were collected to attempt to identify the source of boron which contributed to the formation of B-bearing minerals in the Mendips region, and to help clarify the nature of the mineralization processes that occurred in the area.

## Introduction

The Mendips ore-field (Fig. 1) has been the scene of occasional mining and quarrying activity—concerned principally with the winning of ores of Pb and Zn, and to a lesser extent, those of Mn and Fe—for about two thousand years. The major geological features of the ore-field were described by Green (1958), whilst Gough (1930) presented a comprehensive history of mining in the Mendips.

The Mendips Pb–Zn ores have been studied extensively and, in one such study, Worley & Ford (1977) compared them with other examples of carbonate-hosted Pb–Zn mineralization, particularly the Mississippi Valley type. Models describing this type of mineralization are often based on the migration of metalliferous basinal fluids (Ford 1976; Emblin 1978). However, it is probable that saline groundwaters derived from Triassic sediments were also of importance



**Fig. 1** Simplified geological map of the Mendip Hills, showing the principal localities represented in this study (based on the British Geological Survey 1-inch series, sheet nos 279–281 and Bristol special sheet). D = Downhead; HP = Higher Pitts; M = Merehead Quarry; SSM = Stoke St Michael.

with regard to mineralization in the Mendips, particularly in the formation of the Fe and Mn deposits. Furthermore, interaction of such fluids (or their products) might have led to the formation of the suite of secondary Pb and Cu minerals described by Spencer & Mountain (1923) and Symes & Embrey (1977) which, to date, is unique to the Mendips area.

The association of boron-bearing minerals with some areas of secondary mineralization (Symes 1977) and the paucity of data relating to the geochemical behaviour of B led us to include this element, as well as Li and Be, in the study.

To understand how the Mendips ore deposits and their secondary Pb and Cu minerals were formed, it is necessary to know the distributions and concentrations in the associated country rocks of certain trace elements which could have been the sources of enrichment of groundwaters or other fluids in the past. We have, therefore, sampled and analysed a selection of country rocks, various ore bodies and zones of secondary mineralization in the area.

### Collecting strategy

A total of 37 specimens, which are briefly described in Table 1, were collected for whole-sample analysis from a variety of locations according to the following strategy.

#### Carboniferous Limestone

Campain (1981) presented concentration and distribution data for 15 elements (Ba, Cd, Co, Cu, F, Fe, Li, Pb, Mn, Ni, Cr, Sr, Ti, V and Zn) in Carboniferous Limestone chip samples from the Mendips region. Accordingly, our sampling of Carboniferous Limestone was largely restricted to the mineralized areas.

#### Shales, sandstones and zones of iron-manganese mineralization

Shales, in comparison with sandstones, limestones and evaporites, are relatively enriched in many trace elements, including Cu, Pb and Zn (Wedepohl 1969–78), which occur in the mineralized areas of the Mendips region. Consequently, it is possible that leaching of Palaeozoic shales by Triassic groundwaters could have provided metal-bearing solutions which, under suitable pH and Eh conditions, would have precipitated hydrated oxides of Mn and Fe containing Cu, Pb and Zn.

Therefore, Carboniferous shales and material characteristic of the zones of Mn and Fe mineralization were collected from the Mendips area. The distributions of trace metals in Mn-Fe pods at Merehead Quarry were studied in detail by Thorne (1975), hence many of our specimens were selected to be representative of country rocks associated with the Merehead vein 1 type of formation (see Fig. 2).

The sandstones at Gurney Slade and Stoke St Michael were sampled to complete the coverage of sedimentary rocks.

#### Evaporites

Rankin & Criddle (1985) have shown that low-temperature saline groundwaters derived from Rhaetic-Triassic sediments were involved in iron mineralization in south Wales. Therefore, samples from various Triassic horizons—including evaporites from the Central Somerset Basin (Whittaker 1972) and celestine-rich and siliceous nodules from Dulcote Quarry (Harding 1978)—were collected for analysis.

#### Mesozoic rocks

Although most of the Pb and Zn mineralization is associated with Carboniferous Limestone or Dolomitic Conglomerate, galena and sphalerite-bearing veinlets are present in younger rocks (Rhaetic to Inferior Oolite). The veinlets sometimes continue upward from the Carboniferous rocks into the younger Jurassic rocks (Alabaster 1976; Stanton 1982); consequently these Mesozoic rocks were also sampled.

#### Volcanic rocks

The Silurian andesites of the Beacon Hill pericline and the substantially altered Carboniferous lavas in the Weston-super-Mare area are the only volcanic rocks in the Mendips region. Since

**Table 1** Material submitted to whole-sample analysis. Brief description of specimens 1–37, with locality and National Grid reference.

1. Black Rock Limestone with minor hematite veining. Carboniferous Limestone Series. Vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.
2. Clifton Down Limestone. Carboniferous Limestone Series. Adjacent to galena/baryte vein. Hobbs Quarries, Backwell Hill, Somerset. ST 504684.
3. Black Rock Limestone. Carboniferous Limestone Series. Unmineralized limestone, 4ft from podiform manganese deposit. Vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.
4. Carboniferous Limestone with minor manganese oxide veining. Coombe Farm Quarry, Henbury, Bristol. ST 562778.
5. Silica nodule, 'potato stone'. Keuper Marl, Trias. Dulcote Quarry, near Wells, Somerset. ST 565443.
6. Andesite. Silurian. Moons Hill Quarry, Stoke Lane, Stoke St Michael, Somerset. ST 662461.
7. Dolomitic Conglomerate. Trias. Partially mineralized, *in situ* above adit into old iron mine. Higher Pitts Farm, Priddy, Somerset. ST 534492.
8. Massive gypsum. Trias. Blue Anchor, near Watchet, Somerset. ST 034436.
9. Massive anhydrite (BGS no. 908/02). Trias. Burton Row, Brent Knoll Borehole, Somerset. ST 336521.
10. Massive halite (BGS no. 700/54). Trias. Burton Row, Brent Knoll Borehole, Somerset. ST 336521.
11. Nodular bedded celestine, in Triassic matrix. Yate, Gloucestershire. ST 713835.
12. Massive hematite and goethite associated with secondary Mn/Pb/Cu mineralization. Vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.
13. Galena/baryte vein. Hobbs Quarries, Backwell Hill, Somerset. ST 504684.
14. Massive silica-rich hematite. Winford Quarry, Winford, Somerset. ST 535638.
15. Massive manganese oxides associated with secondary Pb/Cu mineralization. Vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.
16. Massive manganese oxides associated with secondary Pb/Cu mineralization. Higher Pitts Farm, Priddy, Somerset. ST 534492.
17. Limestone. Inferior Oolite. Eastern quarried segment above unconformity. Merehead Quarry, Cranmore, Somerset. ST 695440.
18. Conglomerate (Jurassic) partially overlying vein 1. Merehead Quarry, Cranmore, Somerset. ST 695440.
19. Dolomitic Conglomerate. Trias. Chilcompton Railway Cutting, Chilcompton, Somerset. ST 631512.
20. Nodular bedded celestine. Keuper Marl, Trias. Dulcote Quarry, near Wells, Somerset. ST 565443.
21. Keuper Marl associated with celestine and silica nodules. Trias. Dulcote Quarry, near Wells, Somerset. ST 565443.
22. Upper Coal Measures shale. Writhlington Tip, near Radstock, Somerset. ST 703552.
23. Black Shale. Lower Coal Series, Carboniferous. Edford, Somerset. ST 669488.
24. Lower Limestone Shales. Carboniferous. Roadside cutting near Stoke St Michael, Somerset. ST 669468.
25. Sandstone. Quartzite Sandstone Group. Millstone Grit Series. Gurney Slade, Somerset. ST 632495.
26. Sandstone. Portishead Beds. Old Red Sandstone. Stoke Lane, Stoke St Michael, Somerset. ST 662464.
27. Black Rock Limestone. Carboniferous. Murder Coombe, near Frome, Somerset. ST 743485.
28. Amygdaloidal andesite. Silurian. Downhead Quarry, Downhead, Somerset. ST 688462.
29. Massive manganese oxides. Vein 2, Merehead Quarry, Cranmore, Somerset. ST 695440.
30. White limestone. Rhaetic. Milton, near Wells, Somerset. ST 547473.
31. Copper sulphide vein in Carboniferous Limestone. Vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.
32. Massive manganese oxide. Coombe Farm Quarry, Henbury, near Bristol. ST 562778.
33. Massive goethite (off BM(NH) Min. Dept no. 1971,366). Llanharry mine, mid-Glamorgan, South Wales. ST 015808.
34. Massive hematite. Llanharry mine, mid-Glamorgan, South Wales. ST 015808.
35. Massive goethite. Higher Pitts Farm, Priddy, Somerset. ST 534492.
36. Altered basaltic lava, veined by calcite. Carboniferous. Swallow Cliff, Middle Hope, Weston-super-Mare. ST 324661.
37. Bedded impure limestone overlying vein 1, Merehead Quarry, Cranmore, Somerset. ST 695440.

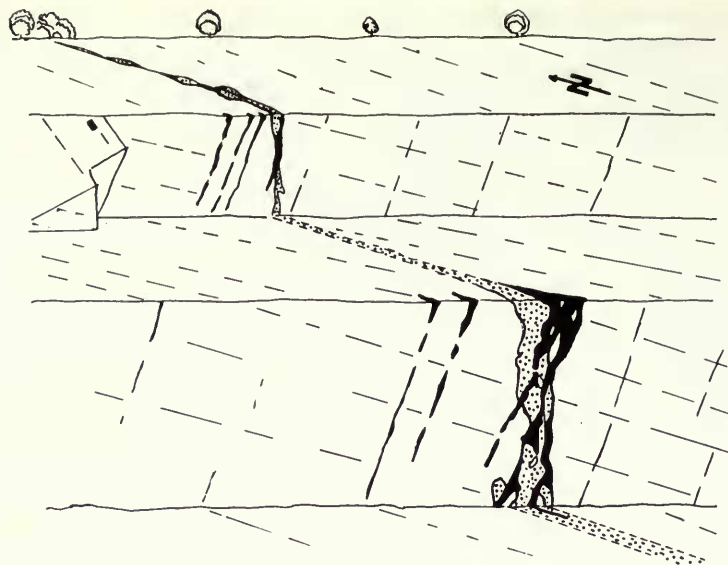


Fig. 2 Field sketch of vein 1, Merehead Quarry, after removal of thin, unconformable cover of oolitic limestone. Note the podiform nature of the vein which has a maximum width of 3.7 metres. Stipple = Mn mineralization; solid shading = Fe mineralization.

volcanic rocks are a possible source of trace-metal enrichment, representative samples of the Mendips volcanics were collected. However, the Cu minerals in the Silurian andesites at Moons Hill Quarry are probably of post-magmatic origin (Van De Kamp 1969).

### Merehead Quarry

In addition to the samples described above, some Mendip mineral assemblages known to contain B-bearing minerals were selected for quantitative B distribution-mapping in order to clarify their relationships with their matrices and to attempt to determine their genesis. Merehead Quarry provides a suitable source of such samples and of material characteristic of zones of Fe and Mn mineralization in the Mendips area.

A representation of vein 1, Merehead Quarry (Symes & Embrey 1977) is shown in Fig. 2. Sampling positions were selected in an attempt to establish patterns of major and trace element contents of the host rocks associated with zones of primary and secondary mineralization in the vein. Some sections of the vein are partially filled by a quartz pebble conglomerate of Jurassic age (as shown by the fossil content) and a friable, leached and partially bedded sediment.

## Techniques

### Chemical analysis

The wide range of compositions of the specimens selected for whole-sample analysis, and the anticipated concentration ranges of the elements to be measured, presented a problem in analytical methodology. There are available several different analytical methods suitable for the quantitative determination of each of the 19 elements originally considered to be of potential interest. It was decided that, if possible, a single technique should be used for all the determinations, so that inter-sample data comparisons would be unaffected by errors that might otherwise be introduced by the use of different preparative and analytical procedures for a given element in different samples.

The relatively new multi-element technique of inductively-coupled plasma emission spectrometry (ICPES) was selected as the most suitable method because it is capable of measuring a

large number of elements—including many, such as B, that are difficult to measure using other techniques—over concentration ranges of several orders of magnitude (Thomson & Walsh 1983).

Because ICPES is essentially a solution analysis technique, it was necessary to find a dissolution procedure effective for all the sample types. The method devised (Din 1984) required successive fusions with potassium dihydrogen orthophosphate and potassium hydroxide. Aqueous extraction of the fusion product yielded a solution which, after acidification, was especially suitable for the determination of B because it was Fe-free. The separation of Fe from B is desirable since spectral interference by Fe with B could require the application of unacceptably large correction factors to the apparent B concentrations measured in Fe-rich solutions. Because some elements are variably distributed between the aqueous extract and the insoluble residue when this procedure is used, to determine the 19 selected elements completely it was necessary to dissolve the residue in dilute nitric acid and analyse this as well as the aqueous extract solutions.

After the ICPES analyses, the Mo content of eight specimens was determined colorimetrically by the method described by Sandell (1959) in an attempt to find areas of enrichment and possible sources of this element, an essential constituent of wulfenite which is sparingly disseminated throughout the Mendips region.

All samples were crushed and ground in agate to  $<150\ \mu\text{m}$  particle size, then dried at  $105^{\circ}\text{--}110^{\circ}\text{C}$  for two hours before being weighed for analysis. The ICPES analyses were made using a Jarrell-Ash Mark III Atom Comp or a Philips PV8210 spectrometer; both instruments were operated at optimum settings for simultaneous multi-element measurements. The accuracy and precision of the method were shown to be acceptable by the analysis of standard reference materials (Din 1984).

### **Boron mapping**

The mineral assemblages selected for B mapping were cut using a wire saw, mounted in epoxy resin, ground flat and finally polished using successively finer grades of abrasive, finishing with  $6\ \mu\text{m}$  or  $1\ \mu\text{m}$  diamond paste. The method of Din & Henderson (1982) was used to generate quantitative B-distribution maps of the specimens. Irradiations were carried out in the vertical thermal column facility of the Imperial College Reactor Centre. Brief descriptions of the specimens together with their measured B contents in ppm by weight are given in Table 2.

## **Results and discussion**

The whole-sample analytical data obtained are summarized in Table 3. The concentrations are quoted in ppm (by weight) except for Al, Ca, Fe, Mg and Si—data for these 5 elements are expressed as weight per cent for concentrations up to 1%. The symbols 'MIN' and 'MAJ' represent the concentration ranges  $>1\%\text{--}<10\%$  and  $>10\%$  respectively. The data for Pb in some specimens are confined to those samples which contain  $>1000$  ppm of the element.

### **The light elements: Li, Be and B**

No definite correlation between the measured concentrations of these three elements was observed. Therefore, it is unlikely that fluids derived from, or associated with, granitic rocks were active in the mineralization processes.

The Li contents of the limestone specimens examined are one to three orders of magnitude lower than those reported by Campain (1981) for limestone chip samples from the Mendips region. However, our data for the element correlate with those in the *Wolfson Geochemical Atlas* compiled by the Applied Geochemistry Research Group (Webb *et al.* 1978) for stream sediments from the area. The highest concentrations of Li in the samples analysed were found in the volcanic rocks, particularly the basic volcanics of the Weston-super-Mare area, with the shale horizons showing some enrichment relative to many of the limestone and mineralized specimens. In general, Be concentrations were uniformly low, with the exception of the possibly significant amounts in specimens no. 2 and 35 (Carboniferous Limestone adjacent to baryte-galena mineralization and goethite respectively).

**Table 2** Boron distribution in some mineral assemblages.

Locality	Sample No.	Description	B content (ppm)
Vein 1, Merehead	B1	Mendipite	5
	B2	Mendipite, chloroxiphite, calcite and Mn-oxides	Mn-oxides 150, others 5-10
	B3	Mendipite and chloroxiphite	5-10
	B4	Chalcosine, malachite and calcite	6-7
	B5	Cerussite, calcite and Mn-oxides	4-6
	B6	Banded Fe-oxides	Goethite 150, hematite 10
	B7	Paralaurionite with mendipite	5-10
	B8	*Mereheadite, mendipite, calcite and *parkinsonite	Mereheadite > 2000, mendipite 10-20, others < 10
	B9	Mereheadite	> 2000
	B10	Mereheadite	> 2000
Vein 2, Merehead	B11	Datolite, apophyllite, calcite and goethite	Datolite > 2000, goethite 350-400, others < 5
	B12	Mereheadite	> 500
	B13	Cerussite and calcite	5-10
	B14	Goethite-Mn-oxide contact	Mn-oxide 10, goethite 100
Merehead, unclassified	B15	Manganocalcite with goethite	Goethite 250, manganocalcite 37
	B16	Wulfenite	< 10
	B17	Mereheadite and chloroxiphite	Mereheadite > 500, chloroxiphite < 10
	B18	Mereheadite, mendipite and calcite	Mereheadite > 500, others 5-10
	B19	Mendipite	5-10
	B20	Hydrocerussite	< 5
	B21	Calcite	5-10
	B22	Cerussite	5-10
	B23	Crednerite	40-60
	B25	Blixite with mereheadite	Mereheadite > 2000, blixite 15-20
Hollybrook	B24	Gypsum and celestine	< 10
Higher Pitts	B26	Mendipite	5-10
	B27	Goethite, hematite and calcite	Goethite 150, hematite 10-20, calcite 5-10
	B28	Hematite and goethite	Goethite 200, hematite 20
	B29	Wulfenite	< 10
Llanharry, South Wales	B30	Goethite	50-100
	B31	Hematite	20
Beckermet, Cumberland	B32	Hematite	25
Nunney	B33	Hematite and goethite	Goethite 120, hematite 20

\* The mineral names 'mereheadite' and 'parkinsonite' have yet to be submitted for approval by the International Mineral Association's Commission on New Minerals and Mineral Names.

Table 3 Whole-sample analytical data, samples 1-37.

No.	Concentration, ppm														Concentration, %													
	B	Ba	Be	Co	Cr	Cu	Li	Mn	Mo	Ni	Pb	Sc	Sr	V	Zn	Al	Ca	Fe	Mg	Si	No.							
1	2	2600	0.8	3	14	33	36	1052		8	3800	<1	338	8	63	0.3	MAJ	MIN	0.5	0.4	1							
2	17	MAJ	1.2	143	102	74	89	52	214	52	214	3	MIN	10	70	0.3	MIN	0.2	0.3	MAJ	2							
3	9	204	1.0	2	25	8	4	42	28	5	28	1	257	2	13	0.1	MAJ	0.02	0.19	0.04	3							
4	19	1253	2.7	659	24	87	77	MIN		75	2185	3	73	25	633	MIN	MAJ	0.8	MIN	MIN	4							
5	<1	291	0.5	13	61	46	12	194	13	24	13	2	752	18	31	0.5	MIN	0.3	0.31	MAJ	5							
6	15	113	1.4	30	206	21	94	1729		100	<5	63	169	180	89	MIN	MIN	MIN	MAJ	6								
7	8	2746	2.6	<1	56	3087	5	8500	11	9	4200	1	206	136	116	0.2	MAJ	MIN	0.16	0.7	7							
8	1	9	0.6	3	8	4	6	2	6	3	6	2	1493	2	2	0.05	MAJ	0.04	0.10	0.3	8							
9	<1	10	0.5	2	6	13	3	<1	12	5	12	2	1323	1	3	0.01	MAJ	0.02	0.005	0.05	9							
10	28	84	0.6	5	18	16	45	111	10	10	14	8	23	18	28	0.7	0.4	0.8	MIN	10								
11	<1	MIN	0.4	<1	5	3	6	28	3	5	14	427	MAJ	6	3	0.3	0.09	0.4	0.06	MIN	11							
12	34	1949	5.1	2	19	406	3	MIN		13	MIN	2	341	109	137	0.02	MAJ	0.06	0.6	0.6	12							
13	<1	MAJ	0.2	21	<1	15	2	90		22	MIN	<1	MIN	1	4	0.01	0.02	<0.001	0.3	0.3	13							
14	62	MIN	7.0	1	8	1	10	3000		12	6	6	2525	3	2	0.05	0.04	<0.001	0.7	14								
15	12	6900	2.5	156	42	3410	3	MAJ	35	38	MIN	1	226	145	118	0.04	MIN	0.06	0.05	0.05	15							
16	17	1378	2.5	127	22	3063	2	MAJ	163	15	MIN	4	52	207	616	0.07	MIN	0.14	0.14	0.2	16							
17	7	1589	1.7	7	<1	12	3	715	<1	20	<1000	6	247	21	29	0.02	MAJ	0.3	0.10	0.5	17							
18	14	303	<1.5	8	17	14	8	892		16	<1000	7	217	55	80	MIN	MAJ	0.7	0.54	MAJ	18							
19	4	1422	<1.5	8	17	14	8	1314		23	<1000	6	141	59	299	0.4	MAJ	0.6	MIN	MIN	19							
20	<1	6251	2.0	7	<1	18	5	2153		20	<1000	8	MIN	27	11	0.05	MAJ	0.5	0.33	MIN	20							
21	27	208	2.0	9	21	29	30	1905		9	<1000	8	463	80	86	MIN	MAJ	MIN	0.86	MAJ	21							
22	42	336	4.0	22	38	41	52	1782		42	<1000	19	95	151	115	MIN	0.5	MAJ	0.86	MAJ	22							
23	39	275	3.7	22	55	33	41	1183	<1	28	<1000	14	74	112	93	MIN	0.4	MIN	0.43	MAJ	23							
24	82	225	3.2	19	59	19	39	860	<1	35	<1000	13	251	105	36	MIN	MAJ	MIN	0.99	MAJ	24							
25	16	113	<1.5	5	128	1	6	<1		<1	<1000	4	32	23	15	0.02	0.07	<0.001	MAJ	25								
26	16	233	<1.5	3	72	7	12	226		<1	<1000	5	22	43	18	<0.01	0.1	0.9	0.19	MAJ	26							
27	8	33	1.0	45	28	68	12	141		64	<1000	4	419	60	92	0.3	MAJ	0.1	0.39	MIN	27							
28	11	100	4.0	64	111	60	66	1103		141	<1000	20	197	165	104	MIN	MIN	MIN	MIN	MAJ	28							
29	17	MIN	5.0	458	<1	2343	10	MAJ	165	165	MIN	3	558	744	405	0.7	MAJ	0.7	0.15	0.3	29							
30	9	50	1.0	45	40	45	13	517		66	<1000	4	464	20	16	0.2	MAJ	0.3	0.30	MIN	30							
31	<1	36	0.3	41	12	MIN	5	532		85	<1000	3	141	24	180	0.05	MAJ	0.2	0.10	0.3	31							
32	163	3253	3.0	625	<1	1102	17	MAJ	555	212	MAJ	3	94	285	1022	0.5	MIN	MIN	0.10	0.3	32							
33	34	28	5.5	78	53	65	3	161		120	<1000	2	11	85	192	0.05	0.2	MAJ	0.05	0.7	33							
34	<1	13	0.3	56	36	41	8	36		76	<1000	2	11	69	113	<0.01	0.03	<0.001	MAJ	34								
35	99	31	14	78	73	67	5	431		134	1282	2	14	176	318	0.05	0.1	MAJ	0.05	MAJ	35							
36	17	35	6	94	251	41	167	431		271	<1000	17	48	198	263	MIN	MIN	MIN	MIN	MAJ	36							
37	<1	84	0.3	39	36	63	12	959		62	<1000	4	126	46	146	0.7	MAJ	0.7	0.17	MIN	37							
Detection limit	1	1	0.1	1	1	1	1	1	1	1	5 or 1000	1	1	1	0.1	0.01	0.01	0.01	0.001	0.01								

MIN = &gt;1 - ≤10% MAJ = &gt;10%

The quantities of B found are unexceptional in terms of average values for limestones and argillaceous rocks (Harder 1974) and no other B-rich areas similar to vein 2, Merehead Quarry (Figs 3a–d), were identified. The element is not associated with the sampled primary sulphide–baryte mineralization, nor is it concentrated in the specimens analysed from the Triassic evaporite suite. Halite from the Brent Knoll Borehole was the only evaporite found to contain a measurable concentration of B.

None of the volcanic rocks (Silurian andesites and altered basic Carboniferous lavas) shows any indication of association with B-rich fluids. However, in general B concentrations are relatively higher in material from the Palaeozoic shale horizons and there is a definite association of B with the goethite of banded Fe oxide mineralization (specimens no. 12, 33 and 35; see also Figs 3a–d) and particularly with the Mn oxide minerals of Coombe Farm Quarry (no. 32).

The B distribution maps (Figs 3a–d) of mineral assemblages from B-bearing zones at Merehead Quarry illustrate graphically the heterogeneity of the distribution of B and provide petrogenetic information on the assemblages. In particular, the B-rich mineral datolite has replaced B-poor baryte (areas I and II, Fig. 3b) and formed large euhedral crystals (areas III and IV, Fig. 3b). The majority of minerals contain less than 10 ppm of B. Those minerals

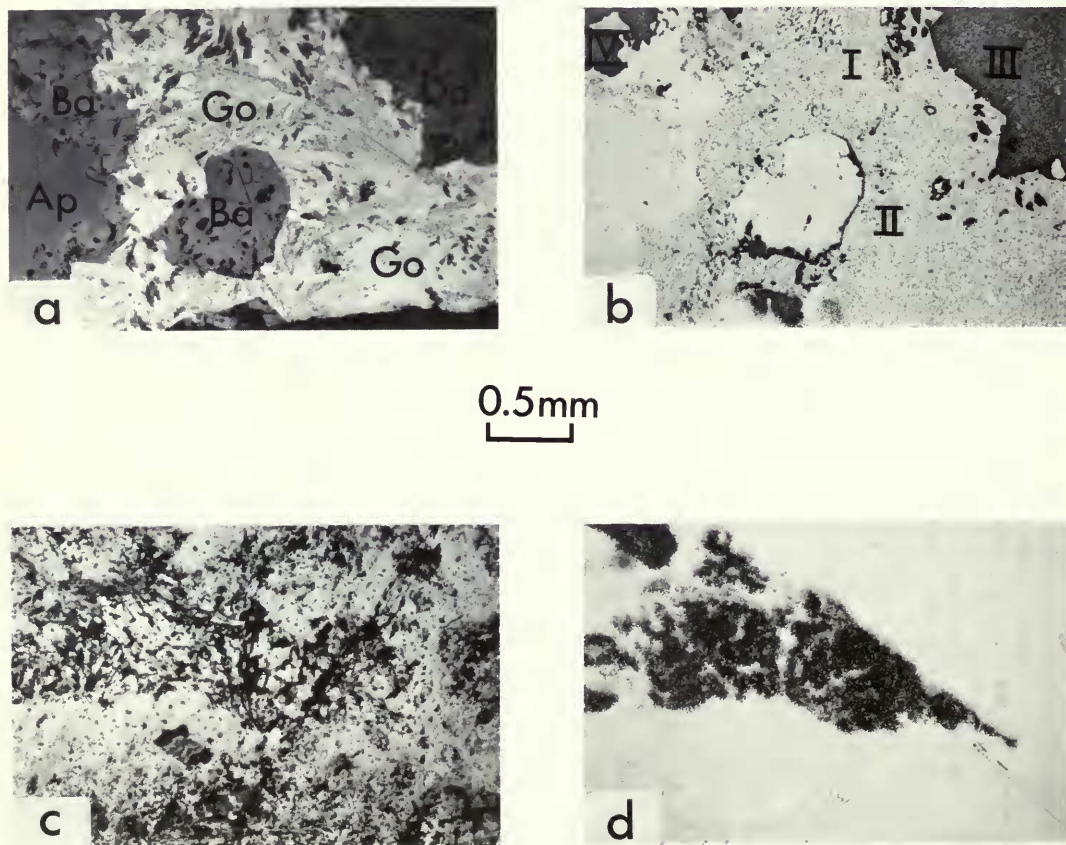


Fig. 3 a, transmitted light photomicrograph of sample B11 from vein 2, Merehead. Ap = apophyllite; Ba = baryte; Da = datolite; Go = goethite. b, B distribution map of the area shown in Fig. 3a. High track densities which correspond to high B concentrations are depicted by the darker areas. The zones marked I–IV are discussed in the text above. c, transmitted light photomicrograph of sample B12 from vein 2, Merehead (mereheadite). d, B distribution map of sample B12. The high track densities reflect the high concentration of B in mereheadite relative to the matrix.



containing more than 10 ppm of the element include mangano-calcite (37 ppm), crednerite (40–60 ppm) and the Pb oxychloride mineral mereheadite (see Table 2), which typically contains >2000 ppm. In contrast, blixite, which is closely related chemically to mereheadite, contains only 15–20 ppm B. The only borosilicate mineral observed in the suite was datolite, which contains approximately 6% of B—too much to be measured accurately under the experimental conditions used to generate the distribution maps.

The Fe oxides goethite and hematite, often intergrown at Merehead, contain significantly different amounts of B. The Merehead goethite specimens carry 150–400 ppm of B, whereas goethite (specimen no. B30) from the Llanharry ore deposit (Gayer & Criddle 1970), which is thought to have been formed in a similar manner to the Mendips iron ores, contains only 50 ppm of the element. Conversely, B concentrations in hematite from Merehead (nos B6, B27 and B28) and from Wales (no. B31) and Cumberland (no. B32) are similar and much less than in the Mendips goethite; all fall within the range of 10–25 ppm.

#### **The alkali earth metals: Sr and Ba**

As might be expected, Sr concentrations in the gypsum and anhydrite specimens (nos 8 and 9) are amongst the highest found within the suite (excluding the celestine deposits). The silica-rich hematite from Winford (no. 14), an area in which celestine is reported, also carries a significant concentration of Sr.

The celestine nodules from the Trias (specimens no. 11 and 20) and the hematite deposits of Winford (no. 14)—where hypogene baryte veins are cut by, and themselves cut, massive Fe ores—are characterized by minor to major Ba contents, and this element is typically present at the thousands of ppm level in Mn and Fe ore deposits. Conversely, the unmineralized Carboniferous Limestones contain only a few hundred ppm of Ba.

#### **Mo and Pb**

From the limited data obtained, the highest concentrations of Mo are associated with the Mn oxide pods which, in some areas, are known to contain wulfenite (Alabaster 1978, Eastwood 1983, Kingsbury 1941, Symes & Embrey 1977). The Carboniferous Limestone at Merehead, the overlying Jurassic rocks and the Palaeozoic shales are all virtually Mo-free, but there is an indication of some enrichment in the Triassic rocks. Pb, like Mo, is associated with the Mn oxide deposits and is a significant constituent of the Mn oxides found in Merehead, Higher Pitts and Coombe Farm Quarries and of the layered Fe oxides at Merehead. This element, together with Ba, is concentrated in the Triassic Dolomitic Conglomerate from Higher Pitts, relative to unmineralized limestone. The Pb (and Ba) contents of the Carboniferous Limestone adjacent to vein 1, Merehead Quarry, are also relatively high, although hand specimens show no evidence of Pb–Ba mineralization.

#### **The transition metals: Sc, V, Cr, Mn, Co, Ni, Cu and Zn**

The Sc concentrations generally correspond with the amounts suggested by Frondel (1970*a, b*) as average for the appropriate sedimentary and volcanic rock types, with the exception of the andesite from Moons Hill (specimen no. 6) in which the element is enriched. The remarkably high concentration of Sc in the Triassic celestine nodule from Yate (specimen no. 11) is not matched by similar or even noticeable enrichment in the other evaporites, or the mineralized specimens in the suite. All the other transition metals, with the exception of Cr, are particularly associated with the Mn oxide deposits. In contrast, Cr, somewhat unexpectedly, is concentrated (relative to the unaltered limestones) in the sandstones from Gurney Slade and Stoke St Michael (specimens no. 25 and 26).

Concentrations of V, Cr and Ni in the volcanic rocks (Silurian andesites and Carboniferous basic lavas) and shales, although unexceptional, are high in comparison with their respective concentrations in the limestones. The vanadate mineral, *vésigniéite*, has been identified from vein 1, Merehead quarry (D. Lloyd, personal communication 1984) where V may have been introduced by manganiferous fluids.

Copper concentrations are high in Mn oxide pods, even where secondary Pb–Cu mineralization is not evident. However, the Cu contents of the volcanic rocks, especially the andesites

from Moons Hill and Downhead, are low, in accord with Van De Kamp's (1969) data and suggestion that the element was introduced into the Moons Hill rock assemblage during a later mineralization.

### Summary and conclusions

The effects of mineralizing fluids on rocks of the Carboniferous Limestone series are confined to fissure channels (characterized by rubbly, discoloured material) and their contiguous rocks. Our very limited survey of the massive, unmineralized Carboniferous Limestones (cf. Campain 1981) shows them to be relatively free of the trace metals associated with zones of Mn-Fe or sulphide mineralization. These rocks in general neither were the source of the trace metals transported by percolating groundwaters, nor were they affected by such fluids.

From the analytical data we obtained, it cannot be adduced that groundwater leaching of Palaeozoic shales in the Mendips region gave rise to the mineralizing fluids which contained the trace elements now associated with the zones of Mn-Fe mineralization. Nevertheless, it is conceivable that the shales were a source of Mn, Fe and possibly other elements including B.

Mn mineralization is a feature of the Triassic rocks (excluding the evaporite assemblages) in the Mendip area, and most of the country rocks in the area are enriched in the element. Our analytical data reflect how Mn oxides have scavenged transition metals from the mineralizing fluids. An exception to this generalization is Cr, which is present at low concentrations in the Mn oxides. Conversely, the concentration of the element in the sandstone samples (nos 25 and 26) is greater than is usual in such rocks (Shiraki 1975).

The Jurassic conglomerate and bedded sediments above vein 1, Merehead Quarry, and the Jurassic Oolitic Limestone which was the original unconformable cover of the vein, contain similar low concentrations of trace elements. Thus it is probable that fissure channels in the area were open to mineralization during the early Jurassic.

Like the shales, the volcanic horizons could have been the source of Mn, Fe and other elements carried by the mineralizing fluids but there is no conclusive evidence to support this hypothesis.

Of the evaporites sampled from the Triassic succession, only halite (no. 10) contains a detectable amount of B. None of the evaporites is remarkable for its trace-element content, except perhaps the nodular celestine (specimen no. 11) which contains over 400 ppm Sc.

The low concentrations of trace elements in the host rocks at Merehead confirm that the mineralizing solutions were restricted to fissure channels. Mn and Fe oxides in the veins show trace-metal enrichment characteristic of other such oxide deposits in the Mendips region, even where specific minerals associated with the enrichment cannot be identified in hand specimens.

The primary Pb and Cu sulphide mineralization in vein 1, Merehead, (Symes & Embrey 1977) was subjected to reaction with pre-Jurassic mineralizing solutions which were rich in Mn and Fe and which transported other metals such as Mo, Co, V and Cu into the area. Under suitable pH conditions and chloride ion concentration (Humphreys *et al.* 1980) a series of rare Pb-Cu oxychlorides were formed by low-temperature reaction between the mineralizing solution and chloride-rich groundwaters which were probably derived from the Triassic sediments.

The source of B, which contributed to the formation of the unique suite of Pb and Cu minerals found in vein 2, Merehead, remains unidentified. A comparatively high concentration of B in the silica-rich hematite deposits at Winford (specimen no. 14) suggests that the silicifying fluids responsible for this late-stage silicification, similar to that which occurred at Merehead (vein 2, particularly), may have been B-bearing. However, if such were the case, then the B-free silica-replaced nodules at Dulcote (specimen no. 5) were probably derived from a different source of silica.

The data presented here do not allow us to propose a genetic model for the mineralization of the Mendips area. However, it is hoped that they will be useful in constraining genetic models of the mineralization which may be postulated in the future. The specimens used for this study are housed in the collection of the Department of Mineralogy, British Museum (Natural History).

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